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jmr&t Journal of Materials Research and Technology

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Original Article

Treatment from abandoned mine landfill leachates. Adsorption technology

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ARTICLE INFO

Article history:
Received 6 June 2018
Accepted 1 April 2019
Available online 25 May 2019

Keywords:
Adsorption
Heavy metals
Red mud
Landfill leachate
Wastewater treatment

ABSTRACT

This study defines the optimal parameters that allow the use of red mud waste from the Bayer process to remove heavy metals from leachate from an abandoned mine. First, the influence of parameters such as pH, contact time, initial metal concentration, adsorbent dose and the presence of co-ions in Cd^{2+}, Zn^{2+} and Ni^{2+} adsorption were investigated in synthetic solutions. Metals uptake increased with increasing pH, contact time and adsorbent dosage. The presence of co-ions suppressed the uptake of heavy metals, divalent ions having a more negative effect than monovalent ions. The adsorption of heavy metals was found to fit the Langmuir isotherm. Maximum Cd^{2+}, Zn^{2+} and Ni^{2+} uptake values were calculated as 12.58 mg/g, 12.05 mg/g and 11.06 mg/g, respectively. The results obtained in the tests with landfill leachate showed that red mud is effective in simultaneously removing several heavy metals, more than 99% Cd, Ni, Zn and As being uptaken.

1. Introduction

The total consumption of aluminum in 2015 was estimated to be 60 million tons, of which 83.3% was produced from primary metal [1].

The most common method for making aluminum is via the Bayer and Hall–Heroult processes. In the Bayer process, bauxite is treated with sodium hydroxide at elevated temperature and pressure in order to dissolve the aluminum, while the other components remain in the solid state (red mud). The amount of bauxite residue produced by this process depends primarily on the type of bauxite (aluminum content, mineral phases) and secondarily on the extraction conditions used by the plant (temperature and pressure) [2,3]. For every tons of alumina extracted, more than a ton of red mud is produced [4].

In recent years, different applications have been investigated for the reuse of red mud rather than its disposal: recovery of iron or rare-earths, as an adsorbent for the removal of toxic pollutants, as an additive to construction materials and ceramic products, as well as for gas cleaning [5–11].

Mining and industrial activities discharge heavy metals into the environment. This pollution has become a global problem due to their toxicity. Furthermore, as these elements are not biodegradable, they tend to accumulate in living organisms [12].

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https://doi.org/10.1016/j.jmrt.2019.04.009

Several treatments have been reported for removing heavy metals from contaminated water: biological processes, adsorption, air flotation, chemical reduction, ion exchange, reverse osmosis, nanofiltration, electrocoagulation, and so on [13,14]. The adsorption method has become one of the preferred processes for removing heavy metals from water as it has been found to be the most efficient and economical technique due to its fast removal rate and minimum pretreatment of samples [15–17].

No reports have been published to date on the relationship between red mud and its ability to remove toxic elements from a leachate from an abandoned mine landfill. The aim of this study is to define the optimal parameters that would enable the use of red mud for removing heavy metal from industrial wastewater.

The leachate under study contains high concentrations of Cd, Zn and Ni, among other contaminants. Tests were initially carried out with synthetic water containing these heavy metals in order to determine the optimal conditions necessary for their removal. Subsequently, tests were carried out with the actual leachate.

2. Material and methods

2.1. Materials

The red mud used in this study was produced at the San Ciprián plant in Spain. This by-product was washed and filtered several times with distilled water to lower the pH to a value close to 8 and was then dried in an oven at 105 °C overnight before use.

The red mud was characterized by different instrumental techniques: X-ray fluorescence (Phillips PW2404), X-ray diffraction analysis (PANalytical ŕPert Pro), surface area (Micromeritics ASAP 2020) and scanning electron microscope coupled with energy dispersive X-ray spectroscopy (SEM/EDX) (JEOL JSM 5600). Particle size distribution was determined by screening. The real density of the red mud was determined using the pycnometer method (UNE Standard 80105), employing water as the immersion liquid (3.67 g/cm^3).

In the synthetic wastewater tests, all the chemical solutions employed were prepared using analytical grade metal sulfates and deionized water. Stock solutions were prepared containing 1000 mg/L cadmium, nickel, and zinc, respectively. Solutions with the desired metal concentrations were prepared by successive dilutions of the stock solution.

The landfill leachate was analyzed by the inductively coupled plasma technique (ICP-MS Agilent 7700), in addition to determining its pH, redox potential and electrical conductivity. Sampling and analysis were in accordance with European standards (EN).

2.2. Batch adsorption experiments

Batch adsorption experiments were carried out by mechanically shaking series of polyethylene bottles containing red mud samples and metal solutions prepared in the laboratory employing an adsorbent concentration of 10 g/L, except in the tests performed to determine the influence of the amount of adsorbent. Samples were shaken at room temperature at 75 rpm, subsequently separating the two phases by filtration. The pH was measured and the metal concentrations in the resulting supernatant were analyzed by atomic absorption spectroscopy.

For each metal solution, one sample was reserved for analysis to determine the initial metal concentration.

The amount of metal removed was determined by mass balances according to Eq. (1):

$$\%\ \text{Metal}_{\text{removed}} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

The amount of metal ion removed by red mud (in milligrams per gram) was calculated according to Eq. (2).

$$q = \frac{(C_0 - C_e) \times V}{W_s} \quad (2)$$

where q is the amount of removed metal ion (mg/g); W_s, the amount of adsorbent (g); C_0 and C_e, the metal ion concentration (mg/L) before and after removal, respectively; and V, the sample volume (L).

Different series of batch experiments were carried out to determine the influence of pH, contact time, initial metal concentration, adsorbent dosage and the effect of other metal ions.

2.3. Adsorption isotherms

In order to investigate adsorption capacity, a series of metal solutions at pH 5 were shaken with red mud for 24 h. Trials were performed with different initial concentrations of 5, 10, 20, 40, 50, 75, 100, 150, 200, 250 and 300 mg/L employing an adsorbent concentration of 10 g/L. The samples were subsequently filtered, and metal concentrations were determined in the liquid phases.

3. Results and discussion

3.1. Characterization of the adsorbent

The chemical and mineral composition of red mud varies depending on the type of bauxite and digestion conditions used in the Bayer process [2,3,18–22].

The chemical analysis determined by X-ray fluorescence showed: 59.89% Fe_2O_3, 7.39%TiO_2, 6.23% Al_2O_3, 2.65% SiO_2, 2.13% BaO, 1.43% CaO, 0.89% SO_3, 7.71% Na_2O, 0.45% K_2O and other elements such as P, Cr and Mn to a lesser extent, with no heavy metals being detected. The loss on ignition (LOI) was calculated by heating a pre-weighed dry sample to 900 °C for 3 h (9.87 wt.%). Sodium and most of the calcium are present as a result of the treatment of the bauxite with caustic soda and lime in the Bayer process [7].

In the XRD characterization using a PANalytical ŕPert Pro system equipped with a Cu source (CuKα), the major crystalline phases present in the red mud were found to be: hematite Fe_2O_3 (ref 01-079-0007), goethite FeO(OH) (ref 01-081-0464) and gibbsite $Al(OH)_3$ (ref 01-074-1775); while the minor crystalline phases present were: kaolinite ($Al_2Si_2O_5(OH)_4$)

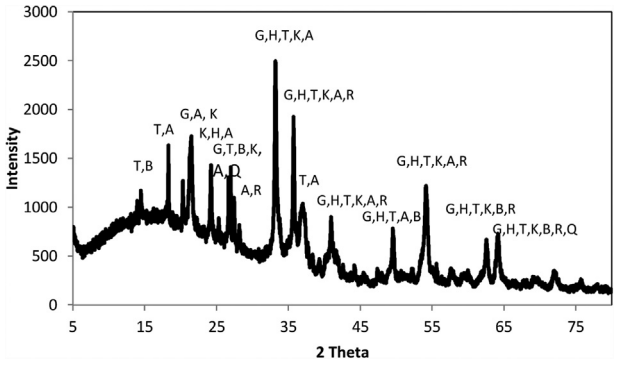


Fig. 1 – X-ray diffraction (XRD) pattern of red mud. G, goethite FeO(OH); H, hematite; T, gibbsite $Al(OH)_3$; K, kaolinite ($Al_2Si_2O_5(OH)_4$); Q, quartz (SiO_2); R, rutile (TiO_2); B, boehmite (AlO(OH); A, anorthite $Ca(Al_2Si_2O_8)$.

(ref 01-072-2300), quartz (SiO_2) (ref 01-089-8934) and rutile (TiO_2) (ref 01-086-0147). Other probable phases were boehmite AlO(OH) (ref.01-088-2111) and anorthite $Ca(Al_2Si_2O_8)$ (ref 01-086-1706), Fig. 1.

The specific surface area was determined by the BET adsorption method. Adsorption isotherm of N_2 at 77 K belongs to type IIb with hysteresis loop type H3 of IUPAC classification [23].

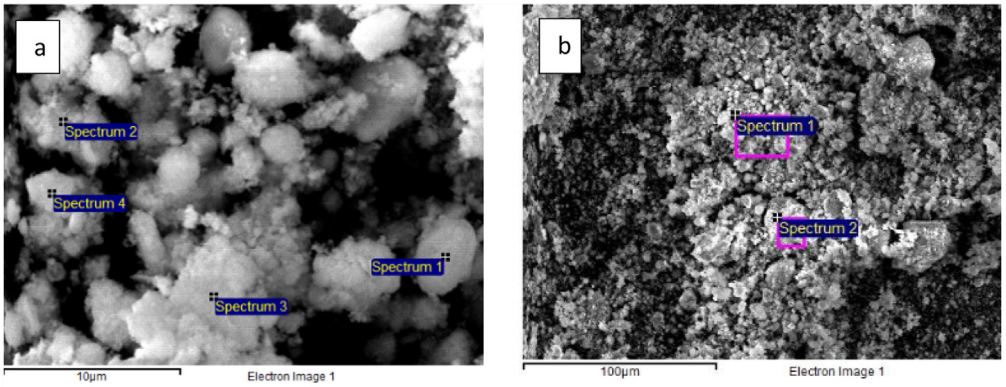
This type of isotherm is assigned to lamellar solids. In this case, its specific surface area (23.8 m^2/g) is relatively high. Also, the CBET value (1 1 0) indicates a typical mesoporous interaction. On the basis of the above, joined to the small curvature toward the ordinate axis, at very high pressures, on the adsorption isotherm, seems to indicate a very high mesoporosity size, as can be seen in the model BJH (Barrett, Joyner and Halenda), although data are in the limit for the application of this technique and therefore should not be taken into account quantitatively, but only as qualitative one.

The scanning electron microscope (SEM) shows that red muds are mixtures of fine, thick and agglomerated particles. Porosity can be also seen in their micrograph, Fig. 2. EDX analysis shows the presence of Fe, O and Al as the major elements, which oxides could be responsible for the adsorption process. Other elements such as C, Na, Si, P, Ca, Cr, Ti and Cu are also detected in smaller proportion.

Red mud is a fine material. It was found to contain 3.8% coarse fraction (>100 μm) and 83.15% within the 53–75-μm range. Around 50% of the particles were found to have diameters below 55 μm, Fig. 3.

3.2. *Characterization of the leachate*

The physico-chemical characteristics of the wastewater were analyzed, the pH (5.18) and redox potential (361 mV) being determined using a PH2002 meter (Crison®) and electrical



Spectrum a	In stats	C	O	Na	Al	Si	P	Ca	Ti	Cr	Fe	Cu	Total
Spectrum1	Yes		38.87	2.30	4.85	1.66			2.24		48.49	1.58	100
Spectrum2	Yes	2.73	30.95	2.63	8.92	1.55		0.84	3.38		17.29	1.71	100
Spectrum3	Yes	3.01	41.88	3.27	8.46	1.96	0.36	1.07	3.04	0.30	35.27	1.38	100
Spectrum4	Yes	2.34	43.58	3.26	5.43	1.16		0.58	2.76		39.62	1.28	100

Spectrum b	Instats	C	O	Na	Al	Si	P	Ca	Ti	Fe	Cu	Total
Spectrum1	Yes	3.47	45.32	2.75	8.39	2.29		0.97	5.19	30.36	1.26	100
Spectrum2	Yes	2.43	36.88	2.03	5.77	1.18	0.52	1.88	2.90	45.32	1.09	100

Fig. 2 – Scanning electron micrograph and EDX analysis of red mud.

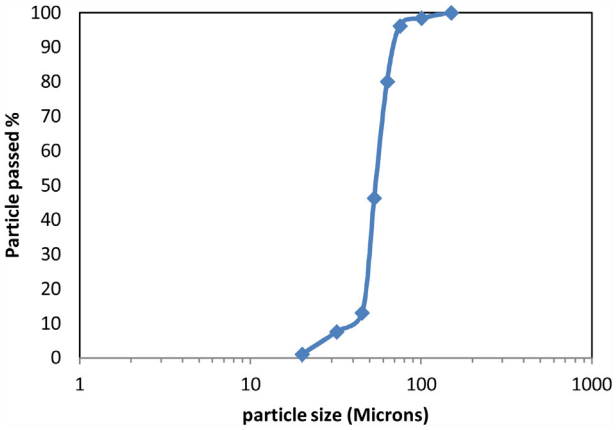


Fig. 3 – Particle size distribution of red mud.

Table 1 – Metal concentrations analyzed by ICP of landfill leachate.

Major component		Minor component	
Element	(ppm)	Element	(ppb)
Ni	18.28	Mn	21.30
Zn	14.41	Cu	15.09
Cd	61.91	Co	0.40
As	6.0	Se	1.94
Na	12,66	V	1.44
Mg	1.49	Ag	4.11
K	19.76	Pb	1.84
Ca	34.22	Sb	25.13
		B	73.8
		Al	545
		Mo	5.21
		Sr	173.5
		Fe	4.70
		Sn	0.44
		Ba	5.96

conductivity (519 μS/cm) using an EC-Meter Basic 30 device (Crison®).

Metal concentrations in the leachate were analyzed by the inductively coupled plasma (ICP) technique, Table 1. The leachate contained significant amounts of heavy metals such as Ni, Zn, Cd and As, in addition to lower amounts of Al, Mn, Sr, Sb, Cu, Se, Fe and Mo.

3.3. *Batch adsorption experiments*

3.3.1. *Effect of pH*

The effect of pH on the adsorption of heavy metal onto red mud was studied by varying the pH of the metal solution over the 2–6 range employing a 50 mg/L metal ions solution concentration and an adsorbent concentration of 10 g/L. The samples were shaken at room temperature at 75 rpm for 3 h.

The heavy metal adsorption capacity onto red mud was significantly affected by increases in pH in the 2–6 range, Fig. 4a. The maximum uptake of ions occurred at pH = 6. The percentage metal ions uptake was found to be respectively 93.2%, 96.0% and 72.1% for Zn^{2+}, Cd^{2+} and Ni^{2+}. Smičiklas et al. [24]

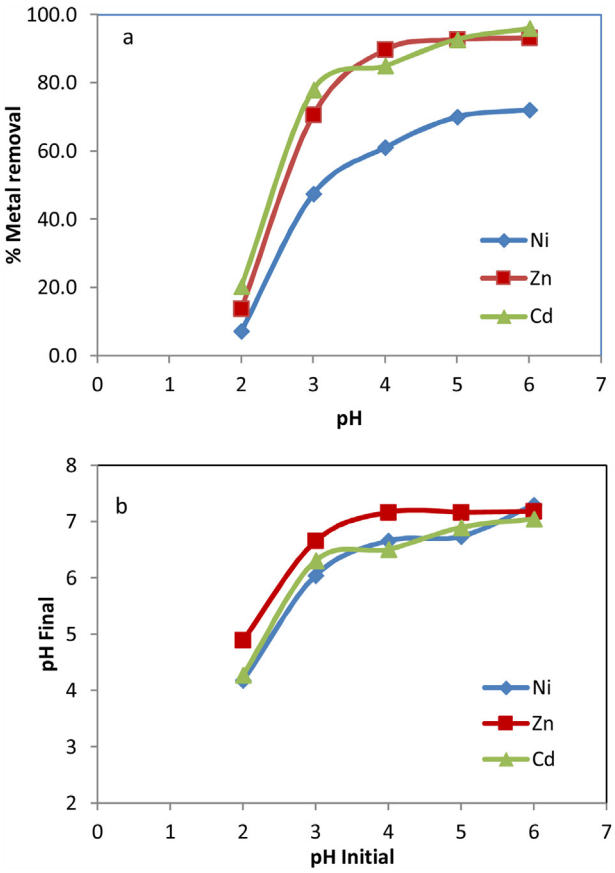


Fig. 4 – Effect of initial pH: (a) % metals removal on red mud and (b) final pH.

reported similar results using red mud activated with acid treatment as the adsorbent.

At lower pH values, the adsorbent surface area is positively charged and the metal ions in solution are positively charged, hence electrostatic repulsion exists between the metal ions and active sites. At higher pH, however, the active sites are negatively charged, there is electrostatic attraction and consequently the removal of heavy metal ions improves under these conditions. The same effect has been reported by other authors using red mud and activated/neutralized red mud [25,26].

The final pH values, Fig. 4b, were in the 4.2–7.3 range in all the cases studied. When the solution comes into contact with the red mud, alkali metals are released and H^+ ions and heavy metals can also compete for the active sites. These two actions will consequently result in an increase in the final pH. As can be seen, red mud has a pH buffering capacity over the ~4–6 pH range.

Metal hydroxide precipitation does not occur; the adsorption of heavy metals onto the red mud surface can be put forward as the most probable mechanism. Santona et al. [27] proposed that Al and Fe oxides and hydroxides, mainly hematite, were the active minerals in the removal of heavy metals due to the fact that the final pH is below the zero point of charge of red muds (pzc 8–8.5). The adsorption of these metals by oxides and hydroxides thus arose via the formation

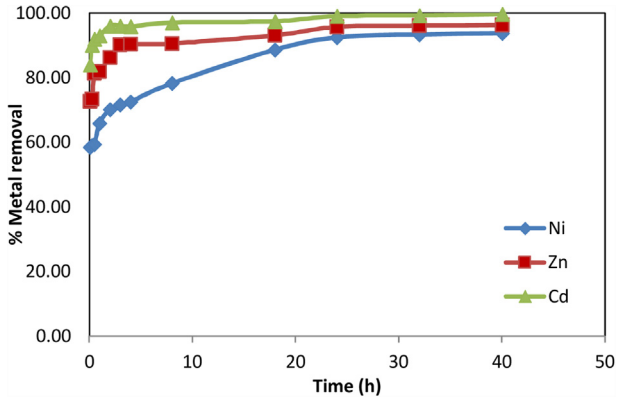


Fig. 5 – % metals removal on red mud versus time.

of specific inner sphere bonds. However, Luo et al. [20] proposed that Cd^{2+} could be adsorbed onto surface hydroxyl groups in Fe- and Al-oxyhydroxide minerals as a mixture of outer-sphere complexes (about 65% Cd) and inner-spheres complexes (about 35%).

As the leachate to be treated in this study has a pH of around 5, the subsequent experiments were conducted at this pH.

3.3.2. *Effect of contact time*

A number of experiments were carried out to examine the influence of stirring time employing an initial metal concentration of 50 mg/L.

The amount of metal ions adsorbed onto red mud was found to increase with time, Fig. 5. Significant removal was observed in the first 5 minutes of contact time, followed by a slower uptake up to 24 h. The surface-active sites of the red mud were initially vacant and the concentration of heavy metals was high. After 5 minutes of contact, many of the functional groups are already linked to the metal ions and therefore the adsorption rate decreases. The maximum rate of metal adsorbed was 95.7%, 99% and 92.4% for Zn, Cd and Ni, respectively, after 24 h stirring time. Therefore, a stirring time of 24 h was chosen to ensure that Zn and Cd adsorption reached equilibrium.

A similar influence has been previously reported for heavy metals adsorption onto untreated [28] and treated red mud: neutralized by seawater [29]; neutralized by CO_2 [26]; and neutralized by acid [18].

3.3.3. *Effect of initial concentration*

The effect of initial concentration was investigated by varying the initial concentration of heavy metals (5–300 mg/L) employing an adsorbent concentration of 10 g/L, Fig. 6.

The results indicate that the percentage of heavy metal removal decreases with increasing initial concentration, Fig. 6a. This is because the available active sites on the surface of the adsorbent tended to be saturated by the metal ions. It was observed that, when employing initial concentrations of 50 mg/L, Cd and Zn were almost completely removed. However, the percentage was lower for Ni, 92%. Removal efficiencies were respectively 40%, 41.7% and 36% for Zn, Cd and Ni when 300 mg/L initial concentration was used.

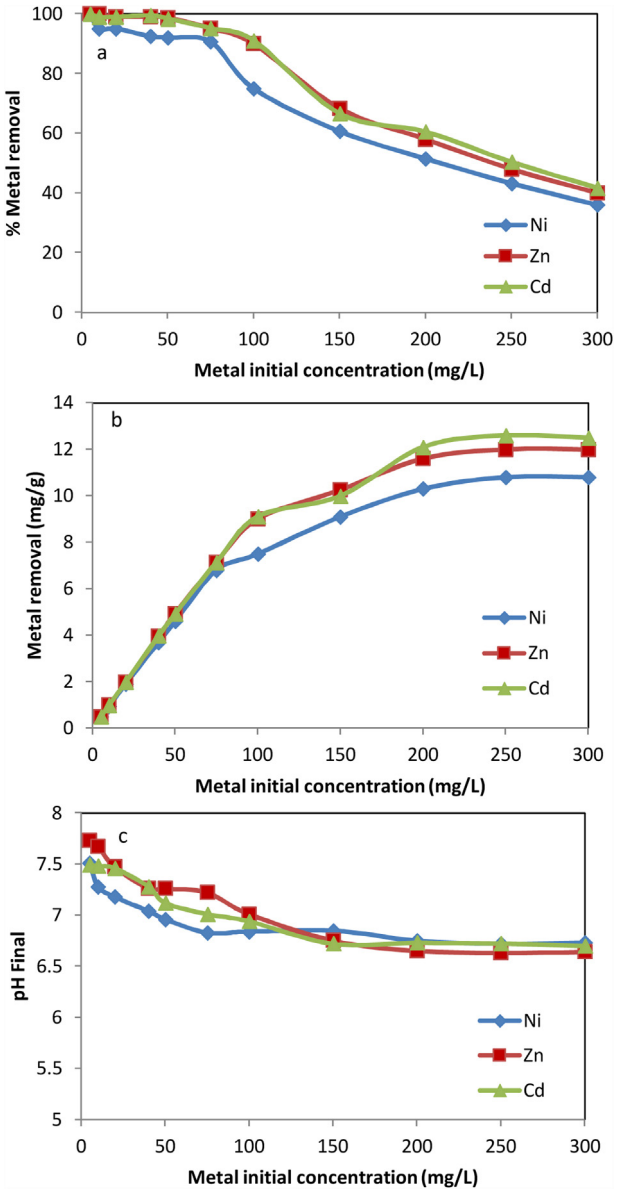


Fig. 6 – Metals removal on red mud versus initial concentration: (a) % percentage of metal removed; (b) metal adsorbed mg/g; (c) pH final.

The amount of metal adsorbed increases linearly from 0.5 to 7.14 mg/g when the initial metal concentration increased from 5 to 75 mg/L, Fig. 6b. With higher initial concentrations, the amount of adsorbed metal is no longer linear. This can be explained by the fact that the adsorbent has a limited number of activated sites and, above a certain concentration, will have become saturated. Nadaroglu and Kalkan [21], and Gupta and Sharma [25] have reported similar behavior for the removal of the Cd, Zn and Co using red mud. As the amount of retained metal increases, the final pH of the solution decreases, thus confirming that H^+ ions are released from the active sites by the formation of inner and outer spheres complexes, Fig. 6c. Luo et al. [20] proposed that the proportion of inner-sphere complexes increases as the concentration of metal in the

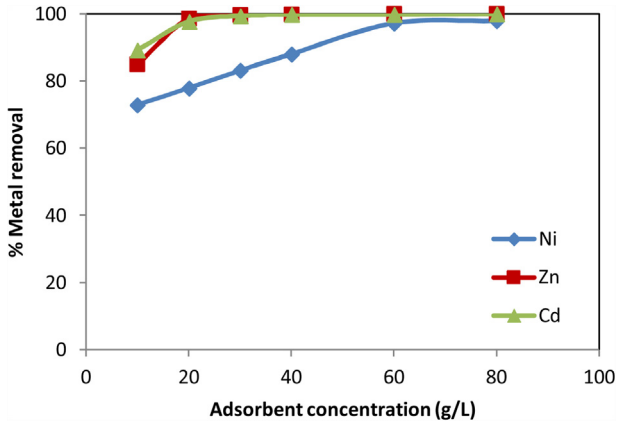


Fig. 7 – Effect of adsorbent dosage versus % metals removed.

solution decreases due to the fact that more hydroxyl groups are available on the surface of the red mud.

3.3.4. *Effect of dosage*

Trials were carried out to study the dependence of heavy metal adsorption on different doses of adsorbent, ranging from (10–80 g/L) using an initial metal concentration of 100 mg/L, Fig. 7.

As can be seen, the amount of adsorbed metals increased progressively with increasing adsorbent dosage. The uptake was over 98% for Zn and Cd when 20 g/L of red mud was used. For Ni, however, 60 g/L of adsorbent was required to achieve the same degree of removal. Similar results have been reported by other researchers: Smičiklas et al. [24] in Ni removal using temperature activated red mud and Sahu et al. [26] in the adsorption of Zn onto neutralized red mud by CO_2. Increases in adsorption with dosage can be attributed to an increased surface area and the availability of more binding sites for adsorption. However, the amount of absorbed metal (mg/g) decreased progressively with increasing adsorbent concentration. Employing an adsorbent concentration of 10 g/L, the amount of metal adsorbed per gram was 7.30 mg/g, 8.50 mg/g and 8.93 mg/g for Ni^{2+}, Zn^{2+} and Cd^{2+}, respectively, whereas the amount of metal adsorbed per gram decreased to 2.77 mg/g, 3.32 mg/g and 3.32 mg/g when employing an adsorbent concentration of 30 g/L. The explanation for this can be found in the flocculation of the solid phase, with the resulting decrease in the available surface area and hence fewer active sites to adsorb the heavy metals.

3.3.5. *Effect of co-ions in solution*

Wastewater in general and the studied leachate in particular may contain different ions that may affect the adsorption of heavy metals onto red mud.

A series of binary solutions at pH 5 were prepared by mixing one of the heavy metals studied here (Zn, Cd or Ni) at an initial concentration of 50 mg/L with different metals (K, Na, Cu, Ca, Mg, Zn, Cd and Ni) at concentrations ranging from 5 to 50 mg/L. The experiments were performed under the same conditions as in the previous trials.

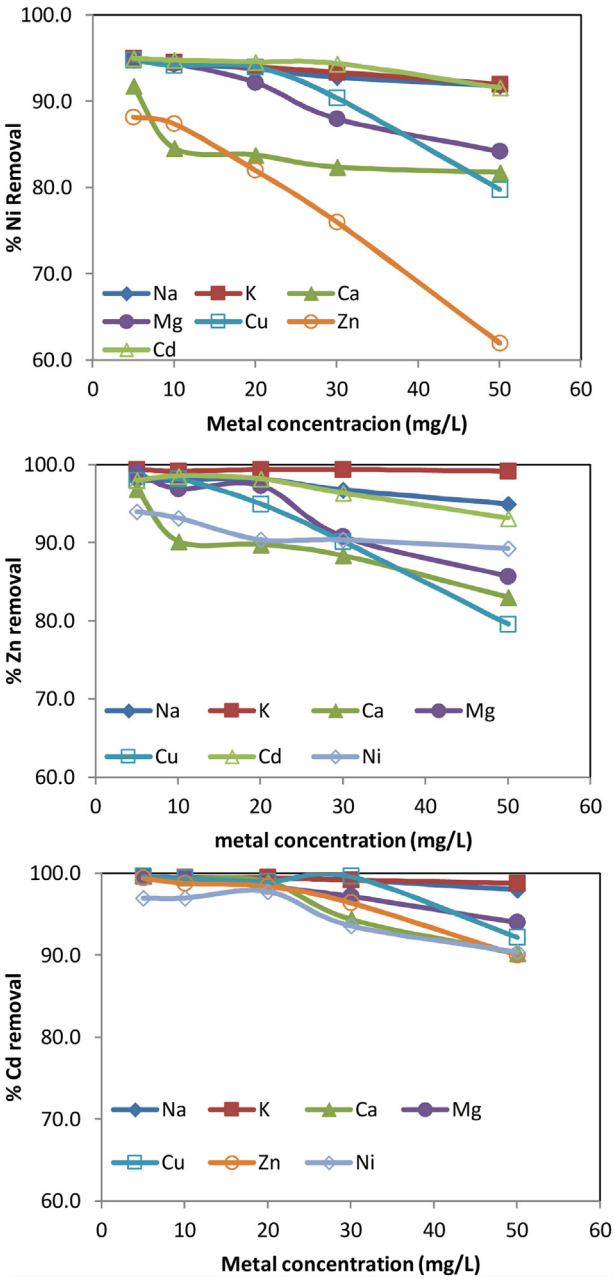


Fig. 8 – Influence of other metal ions in Zn, Cd and Ni removal on red mud.

The adsorption of metal ions decreased with increasing concentration of other metal ions, Fig. 8; this is because more cations can compete for the active sites on the adsorbent surfaces. This phenomenon is more noticeable the greater the concentration of the co-ion, as many of the active sites were occupied by these ions. Ni was the metal most affected by the presence of co-ions, and Cd the least.

The presence of Na^+ and K^+ was not found to have a significant effect on the removal of heavy metals. Ni and Cd removal efficiencies decreased 26.2% and 9.4%, respectively, when using a concentration of 50 mg/L Zn in the solution. This is because sorption of monovalent ions is usually non-specific

Table 2 – Langmuir and Freundlich adsorption isotherm constants.

Metal	a_{max} (mg/g)	b (L/mg)	R^2	ΔG° (kJ/mol)	K	n	R^2
Ni	11.062	0.167	0.997	−22,540	2.08	2.76	0.878
Zn	12.048	0.517	0.998	−25,616	4.40	4.50	0.886
Cd	12.579	0.411	0.996	−26,344	3.79	6.68	0.833

and monovalent-ion selectivity is generally much lower than that of multivalent ions.

The negative effect of co-ions on metals uptake followed the order below:

$$\text{Znremoval}: K < Na < Cd \approx Ni < Mg \approx Ca < Cu$$

$$\text{Cdremoval}: K < Na < Mg < Ni < Cu < Ca \approx Zn$$

$$\text{Niremoval}: K \approx Na \approx Cd < Ca \approx Mg < Cu < Zn$$

The pH_{final} values after heavy metal adsorption varied little depending on the presence of co-ions (0.2–0.3), in most cases. The pH_{final} never exceeded the value of 7.5.

3.4. *Adsorption isotherms*

In order to describe metal adsorption behavior onto red mud, the isotherm data were fitted to the Langmuir adsorption model.

The Langmuir adsorption isotherm is applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites. The Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{ba_{max}} + \frac{C_e}{a_{max}} \quad (3)$$

where C_e is the equilibrium concentration of the metal ion in solution (mg/L); q_e, the amount of metal adsorbed at equilibrium (mg/g); while b and a_{max} are Langmuir constants related to the binding constant and the maximum adsorption capacity, respectively. The values were estimated from the intercept and slope of the regression line for different initial metal concentrations.

The essential feature of the Langmuir isotherm can be expressed in terms of the dimensionless separation parameter, R_L. This parameter is indicative of the isotherm shape, which predicts whether an adsorption system is favorable or unfavorable. R_L is defined as:

$$R_L = \frac{1}{n(1 + bC_0)} \quad (4)$$

where b is the Langmuir constant; and C_0 is the initial concentration. The R_L value indicates the shape of the isotherm as follows: unfavorable ($R_L > 1$); linear; favorable ($0 < R_L < 1$); or irreversible ($R_L = 0$) [25,26].

The adsorption data were also tested using the Freundlich isotherm equation:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (5)$$

where q_e is the amount of metal adsorbed at equilibrium (mg/g); C_e, the equilibrium concentration of the metal ion in solution (mg/L); K, the equilibrium constant indicative of adsorption capacity; and n is the adsorption equilibrium constant. If the value $1/n$ is below unity, this implies that the sorption process is chemical; if the value is above unity, sorption is a favorable physical process.

Adsorption parameter values are given in Table 2. Results showed that the adsorption data could fit Langmuir equation according to the correlation coefficients obtained for the heavy metals studied in this work. The data showed that the maximum adsorption capacity for heavy metals, a_{max}, was 11.06 mg/g, 12.05 mg/g and 12.58 mg/g for Ni^{2+}, Zn^{2+} and Cd^{2+}, respectively. Smičiklas et al. [18] reported 11.11 mg/g maximum adsorption capacity for Ni when using acid-activated red mud.

The adsorption capacity values of this red mud are relatively small compared to other materials such as clays. Several researchers have found that depending on the clay used the adsorption capacity of Cd removal varies between 3.87 mg/g and 971 mg/g and between 2.64 mg/g and 250 mg/g for Zn removal. This may be due to the fact that the clays have a small particle size and a complex porous structure with a high specific surface area, which allows strong physical and chemical interactions with dissolved species [30].

The R_L values for adsorption onto red mud at an initial concentration of 5 mg/L were 0.545, 0.279 and 0.327 for Ni, Zn and Cd, respectively, while at 300 mg/L the values vary between 0.020 and 0.006. The data thus obtained represent favorable adsorption.

The standard Gibbs free energy changes (ΔG°) for the adsorption process can be calculated using the following equation:

$$\Delta G^\circ = -RT \operatorname{Ln} b \quad (6)$$

where b is Langmuir constant, R is the gas constant and T is the temperature. The negative free energy values indicate that the process is both viable and spontaneous.

3.5. *Treatment of landfill leachate*

Experiments were carried out at different reaction times using adsorbent concentrations of 5 g/L and 10 g/L under the same conditions as in the previous trials.

The leachate reached a pH value of 6.5 and 6.3 after 5 minutes of treatment for an adsorbent concentration of 10 g/L and 5 g/L, respectively, reaching a pH value of 6.7 after 24 h with both adsorbent concentrations.

Metals removal is very fast, beginning shortly after stirring commences, and increases over time, Fig. 9a. Percentage removal efficiency values were 47.2%, 86.7%, 75% and 97.5% for Ni, Zn, Cd and As, respectively, after 4 h of treatment. No

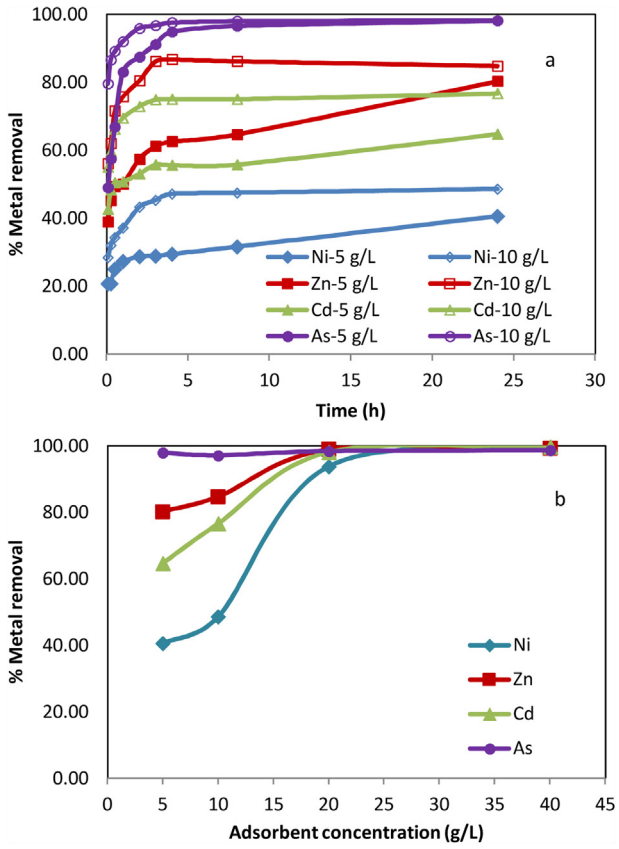


Fig. 9 – Treatment of leachate using red mud: (a) effect of time and (b) effect of adsorbent dosage.

further adsorption was obtained with further stirring time when using an adsorbent concentration of 10 g/L. A longer stirring time (24 h) was required to reach maximum efficiency when employing a lower adsorbent concentration of 5 g/L.

The percentage metal removal from the leachate is lower than from synthetic solutions. This may be due to the fact that the leachate has metal ions that can react with the adsorbent surface. In the tests carried out with co-ions, it was found that the presence of Na^+ and K^+ did not have a significant effect on the removal of heavy metals. However, Zn, Cd, Ni and Ca removal efficiencies decreased. It should be borne in mind that the influence of co-ions was studied in metallic binary system solutions and leachate is a metallic multicomponent system. Moreover, the studies on synthetic solutions did not consider the influence that the presence of other non-metallic ions and biological activity may have on the adsorption mechanisms of the studied heavy metals.

The results obtained in the removal of As were as expected, given that several investigators had reported As removal in synthetic wastewater using neutralized and activated red muds [31,32]. Fe and Al oxides and oxyhydroxides were probably the mineralogical phases involved in As uptake. Castaldi et al. [33] proposed that As adsorption by red mud involved the formation of inner-sphere complexes.

Trials were performed employing a different adsorbent dosage, Fig. 9b. The metals removal rate gradually increased as the dosage of adsorbent increased, achieving almost complete removal of heavy metals. After treatment with a concentration of 10 g/L, the concentrations of Ni, Zn Cd and As in the leachate were 9.5 mg/L, 2.4 mg/L, 15.48 mg/L and 169 μg/L, respectively. When the adsorbent concentration was increased to 40 g/L, the concentrations of these metals varied between 129 μg/L Cd and 78 μg/L As.

After treatment with red mud, the concentration of Fe, Cu, Co and Mo also decreased in the leachate.

The rapid removal observed in these tests shows that it is possible to carry out an efficient and economical treatment of the leachate using red mud.

4. Conclusions

Metals uptake is a function of pH, contact time, initial metal concentration, adsorbent concentration and co-ions. The optimum solution initial pH was found to be 6, the maximum uptake at this pH being 93.2%, 96.0% and 72.1%g for Zn^{2+}, Cd^{2+} and Ni^{2+}, respectively, in synthetic solutions. Metals uptake was found to be very rapid, over 90% Cd and Zn removal being obtained in the first 3 h. Heavy metal concentrations can be reduced by increasing the adsorbent dosage. The presence of co-ions suppressed the uptake of heavy metals, divalent ions having a more negative effect than monovalent ions.

The adsorption isotherms data fitted the Langmuir isotherm model, with R^2 correlation coefficient values between 0.998 and 0.996. Furthermore, the maximum Zn, Cd and Ni uptake values were calculated at 12.05 mg/g, 12.58 mg/g and 11.06 mg/g, respectively. The negative free energy values indicate that the process is both viable and spontaneous.

The present study shows that it is possible to carry out an efficient and economical treatment of landfill leachate using red mud. This treatment is effective in simultaneously removing various heavy metals such as Ni, Zn, Cd and As. Heavy metals concentrations present in the leachate before treatment were 14.41 mg/L Zn, 61.91 mg/L Cd, 18.28 mg/L Ni and 6.0 mg/L As, while after treatment with 40 g/L adsorbent, the concentrations were 96.2 μg/L Zn, 129 μg/L Cd, 111.4 μg/L Ni and 78 μg/L As.

Conflicts of interest

The authors declare no conflicts of interest.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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